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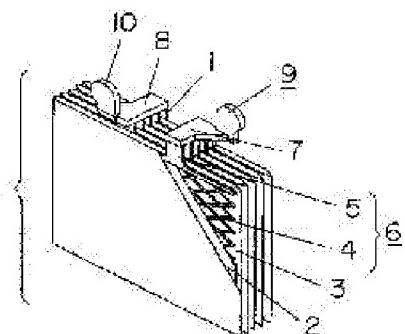
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(54) LEAD-ACID BATTERY

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a highly reliable lead-acid battery by suppressing corrosion of a negative electrode tab part, suppressing increase of the liquid reduction amount, and securing charging power largely affecting the service life characteristics.

SOLUTION: A positive electrode member comprising a positive electrode grid, a positive electrode shelf 8, a positive pole, and positive electrode connecting body 10 is composed of lead or lead alloy substantially including no Sb. A part excluding a negative electrode grid skeleton part out of a negative electrode member comprising a negative electrode grid 6, a negative electrode shelf 7, a negative pole, and a negative electrode connecting body 9 is composed of lead or lead alloy substantially including no Sb. Either one of the negative electrode grid skeleton part or a negative electrode active material includes Sb and the content of the Sb to the amount of the negative active material is 0.001-0.1 mass%.



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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention]Especially this invention relates to the lead storage battery which does not contain antimony (Sb) in the member which constitutes an anode.

[0002]

[Description of the Prior Art]Although the Pb-Sb alloy was used for the positive electrode lattice body of the conventional lead storage battery, there was a problem that **** was not mostly excellent in a conservation characteristic etc. As this reason, when the charge and discharge of the lead storage battery are carried out, it is because Sb gradually contained in the positive electrode lattice body is eluted, the hydrogen overpotential in a negative electrode falls by Sb which deposited and deposited in the negative electrode and it becomes easy to generate hydrogen gas. If the charge and discharge of a cell are furthermore performed continuously then, Sb precipitation amount on a negative electrode will increase, and **** will advance further. Even if **** advances, when water refilling is neglected, a negative electrode ledge and a negative-electrode handle part are exposed from an electrolysis solution. Once these negative electrode members were exposed from the electrolysis solution, corrosion advanced rapidly, and there was a problem which results in a short life.

[0003]

[Problem(s) to be Solved by the Invention]In order to control a short life by such corrosion and this in recent years, to the positive electrode lattice body, the cell with the outstanding maintenance free nature using the Pb-Ca-Sn alloy which does not include the parenchyma top Sb has become common. However, using the Pb-Sb alloy containing Sb for the anode pillar or anode connection body which drew the anode board from the anode shelf which carries out a cluster weld, or the shelf has generally been performed.

[0004]Although low water loss falls substantially as compared with the storage battery by which the storage battery using Pb alloy which does not contain Sb in a positive electrode lattice body used the Pb-Sb alloy, it has turned out that there is a tendency in which Sb contained in the shelf, pole pillar, and connection body of an anode in the end of life of a storage battery carries out a segregation to the portion centering on a negative-electrode handle part. When the negative-electrode handle part in which such Sb carried out the segregation was exposed from an electrolysis solution, corrosion advanced on the surface of a negative-electrode handle part and thickness became thin, the technical problem that the intensity of a handle part will fall occurred.

[0005]

[Means for Solving the Problem]In order to solve said technical problem, an invention of claim 1 of this invention has the anode board provided with a positive electrode grid which consists of a negative electrode plate provided with a negative electrode grid which consists of a lattice handle part and a lattice bony septum, a lattice handle part, and a lattice bony septum, In a lead storage battery provided with a pole pillar or a connection body drawn from a shelf which carries out the cluster weld of the polar-plate handle part of like-pole nature, and this shelf, A positive electrode member which comprises a positive electrode grid, an anode shelf, an anode pole pillar, and an anode connection body consists of lead or a lead alloy which does not contain the parenchyma top Sb, A part except a negative electrode grid bony septum consists of lead or a lead alloy which does not contain the parenchyma top Sb among negative electrode members which comprise a negative electrode grid, a negative electrode ledge, a negative-electrode pole pillar, and a negative-electrode connection body, A lead storage battery with which either one of a negative electrode grid bony septum or negative electrode active material is characterized by content to the amount of negative electrode active material of said Sb being 0.001 to 0.1 mass % including Sb.

[0006]A lead storage battery, wherein content to the amount of negative electrode active material of said Sb is 0.001 to 0.1 mass % is shown including Sb.

[0007]An invention concerning claim 2 of this invention shows a lead storage battery, wherein content to negative electrode active material of this Sb is 0.001 mass % - 0.02 mass % to negative electrode active material in a lead storage battery of claim 1 including Sb.

[0008]An invention concerning claim 3 of this invention shows at least a lead storage battery provided with a lead alloy layer of the surface which touches positive active material of a positive electrode grid in claim 1 or a lead storage battery of 2 which contains Sn not less than 2% in part.

[0009]

[Embodiment of the Invention] The lead storage battery by an embodiment of the invention is explained using a drawing.

[0010] Drawing 1 is a **** figure showing the group of electrode 1 which constitutes the lead storage battery of this invention. The anode board (not shown) has the composition with which the active material was filled up into the positive electrode lattice body which comprises the anode handle part 1 and a positive electrode grid bone (not shown). This anode board and negative electrode plate 2 have countered mutually via the separator 3.

[0011] The negative electrode plate 2 has the negative electrode grid object 6 which comprises the negative-electrode handle part 5 and the negative electrode grid bone 4. The cluster weld of the handle parts of like-pole nature is carried out, the anode shelf 8 and the negative electrode ledge 7 are formed, respectively, and a pole pillar or a connection body is formed in each shelf. the example shown in drawing 1 -- an anode and a negative electrode -- each -- the example which formed the anode connection body 8 and the negative-electrode connection body 9 is shown in the shelf.

[0012] In this invention, the anode handle part 1, a positive electrode grid bone, the anode shelf 8, the anode connection body 8, and an anode pole pillar (these are named generically and it is a positive electrode member) consist of Pb(s) or Pb alloys which do not include the parenchyma top Sb. However, Sb contained as an about several ppm impurity removes. Since oxidization corrosion advances in an anode, it is preferred to use Pb-Sn alloy.

[0013] On the other hand, about a negative electrode, the negative-electrode handle part 5, the negative electrode ledge 7, the negative-electrode connection body 9, and a negative-electrode pole pillar consist of Pb(s) or Pb alloys which do not include the parenchyma top Sb like a positive electrode member. However, even if there is little negative electrode grid object 6 or negative electrode active material, it constitutes so that Sb may be included in either. When making a negative electrode grid object contain Sb, in constituting the negative electrode grid object 6 from a Pb-Ca alloy especially in a maintenance free cell, on the layer and concrete target which contain Sb in a Pb-Ca alloy surface, it arranges a Pb-Sb alloy layer. In making Sb contain in negative electrode active material, it adds Sb to raw material lead powder of an active material.

[0014] The amount of Sb(s) added in this invention in the negative electrode grid object 6 or negative electrode active material is limited to the range of 0.001 mass % - 0.1 mass % to the amount of negative electrode active material. using such a group of electrode -- a law -- the lead storage battery of this invention can be obtained by assembling in accordance with a method.

[0015] When adding Sb especially to negative electrode active material, the addition of 0.001 - 0.02 mass % is preferred to the amount of negative electrode active material. It is preferred to arrange the Pb-Sn alloy layer of the surface which contacts the positive active material of a positive electrode lattice body preferably which contains Sn more than 2 mass % in part at least.

[0016] The cell by the composition of this this invention controls the increase in **** at the time of the life cycle which is the technical problem mentioned above, and cancels the corrosion in a negative electrode, and contributes the outstanding life performance.

[0017]

[Example] The cell by the example of this invention and a conventional example was created, and evaluation of the existence of the corrosion of low water loss and a negative-electrode handle part and charge acceptance nature was performed by doing a overcharge examination and an overdischarge examination.

[0018] Alloy composition is Pb-0.07 mass %Ca-1.3 mass %Sn, using a Pb-Ca-Sn alloy in the positive electrode lattice body of the lead storage battery of this invention. After rolling this alloy (sheet 1) gradually, expanded processing was performed and the lattice body was formed, and it was filled up with active material paste, and the anode board (P1) was produced. The Pb-7 mass % Sn alloy (sheet 2) about 0.2 mm thick was piled up on the sheet 1, it rolled gradually, and the anode board (P2) was produced through the same process as henceforth. On the other hand, the negative electrode plate created the lattice body through expanded processing, after rolling the Pb-0.07 mass %Ca-0.25 mass % Sn alloy (sheet 3) like the anode. Then, the lattice body was filled up with the active material paste which did 0.010 mass % addition of Sb to the amount of active materials, and the negative electrode plate (N1) was obtained. The Pb-2 mass %Sb alloy (sheet 4) about 0.2 mm thick was piled up on the sheet 4, it rolled gradually, and the negative electrode plate (N2) was produced through the same process as henceforth. In the separator, the saccate separator of the form where an anode board is wrapped in was produced using the sheet made from microporous polyethylene about 0.3 mm thick.

[0019] The lead storage battery for cars of 55D23 type (12V48Ah) was produced using the group of electrode which comprises five anode boards per one cell, and six negative electrode plates using two kinds of above-mentioned anode boards, and two kinds of negative electrode plates. When forming a group of electrode, it was made the connection body which joins between the shelf which connects the polar plate in an anode, and a cell with the composition which does not contain Sb in the whole anode using the alloy which does not contain Sb.

[0020] It piled up (it is based on the conventional manufacturing method) for comparison, the Pb-7 mass %Sb alloy (sheet 5) about 0.2 mm thick was piled up on the sheet 1, it rolled gradually, and the anode board was produced through the same process as henceforth (P0). The negative electrode plate rolled the sheet 3 gradually, and produced it through the same process (N0). The cell of the composition using this lattice body was used as the cell of a conventional example. The conditions of detailed battery construction are shown in Table 1.

[0021]

[Table 1]

電池 No	電池構成			①過充電試験		②過放電試験
	正極の 錫-格子体	正極格子体上の 表面層	錫板内のSb	減容量	直接導電率(初期に 及ぼす割合)	充電挿入性
従来例 A	Sbあり	Pb-Sn合金(P1)	なし(NC)	100%	82%	100%
本発明例 B1	なし(BL)	なし(P1)	溶物質に含蓄(N1)	73%	99%	92%
	なし(BL)	なし(P1)	錫子板上の 表面層に含蓄(N2)	70%	98%	43%
	なし(BL)	Pb-Sn合金(P2)	溶物質に含蓄(N1)	79%	98%	98%
	なし(BL)	Pb-Sn合金(P2)	錫子板上の 表面層に含蓄(N2)	68%	98%	102%

[0022]<< examination 1>> -- in order to evaluate the corrosion in the low water consumption and the negative electrode which are technical problems about the cell of composition of differing respectively, life test of the following patterns was carried out. This life test is a test pattern supposing how a overcharge tendency is used, and repeated the cycle which performs 13.8V constant potential charge continuously in 75 ** atmosphere for 120 hours. In order to assume the state where **** advanced and the polar-plate upper part was exposed from the electrolysis solution, it examined, where an electrolysis solution is reduced to the minimum level. Then, removal and measurement of negative-electrode ear thickness were performed for the corrosion product generated on the negative-electrode ear surface, and it asked for the ratio of the ear thickness after the test termination to the ear thickness of an initial state by percentage.

[0023]This test result is shown in Table 1. The life test evaluation in a table compared the cell which sets to 100 the low water loss and the corrosion rate of the cell A which consist of the conventional composition, and consists of each composition. It is the composition which the cell A of a conventional example contains Sb on the connection body of a part as shown in drawing 1 in an anode, a shelf, and the lattice body surface, and does not contain Sb in a negative electrode. On the other hand, the cells B1-C2 of this invention are cells of composition of that each cell contains Sb at a negative electrode excluding Sb in an anode. It was a result with as little [for the examples B1-C2 of this invention] low water loss to the conventional example A as [about about 70 to 80 percent]. Although especially the conventional example A had little **** in the first stage, when the cycle advanced, the tendency for **** to increase gradually was seen. Sb contained in the anode is eluted and this deposits in a negative electrode as a cycle advances, and it is considered to originate in hydrogen overpotential falling and hydrogen gas being emitted. Although there are also few Sb precipitation amounts from an anode to a negative electrode the first stage, it is thought that Sb precipitation amount also increased gradually with cycle advance, and **** increased. On the other hand, this inventions B1-C2 are eliminating Sb of an anode and giving very small quantity Sb beforehand to a negative electrode, and can be assumed to be the results which canceled increase of **** accompanying cycle advance and have been controlled to moderate low water loss. In B1 and B-2, there was slightly much low water loss of B1. Although this reason is not clear, since Sb exists on negative electrode active material, B1 can consider that the reaction surface area on Sb is wide range than B-2.

[0024]In B1-C2 which are examples of this invention, corrosion was not seen at all, but the conventional example A was in the same state as the first stage, although advance of corrosion was seen in the negative electrode ledge part and the handle part. It can be guessed that Sb contained in the anode of the conventional example A originates as this reason. As mentioned above, although Sb of an anode is eluted with cycle advance and deposits in a negative electrode, it deposits in the upper part considered that reaction availability is high also within a polar plate mostly. It is presumed that Sb carries out a segregation to the shelf, polar-plate handle part, and cope box bone which are not covered in particular with an active material (the handle part and cope box bone of a negative electrode plate are shown in drawing 2). According to cycle advance, the part in which Sb carried out the segregation is exposed, and the surface is considered that it is covered with thin liquid membrane and pH increases. Then, the dissolution of Pb takes place easily according to pH increase, on Sb, hydrogen gas is emitted, the local cell which Pb dissolves on Pb and lead sulfate generates is formed, and it is guessed that corrosion is advancing. On the other hand, without being eluted to an electrolysis solution and depositing in the negative-electrode upper part, since the examples B1-C2 of this invention do not contain Sb in the anode, even if electrolysis solutions decrease in number and the negative-electrode upper part is exposed, in order not to form a local cell, it is thought that corrosion did not advance, and it can be said that corrosion is prevented. The difference was not looked at by corrosion in the examples B1-C2 of this invention. It can say that it is because Sb of an anode is eluted also from this as for corrosion and it deposits to the negative-electrode upper part, and it is thought by the cell which Sb does not contain in an anode that a difference was not seen.

[0025]The examination which assumed overdischarge neglect apart from << examination 2>>, next the life test supposing the above mentioned overcharge tendency was done. After this test condition carried out constant current discharge by 9.6A for 5 hours, it connected the load of 10W in 40 ** atmosphere, discharged it for 14 days, removed load, made it the open state, and was exceedingly neglected for 14 days in 40 ** atmosphere. Then, after carrying out recovery charge by 15.0V for 4 hours, 5 hour-rate discharge estimated capacity. This test result is shown in (Table 1). The test evaluation in a table compared the cell which sets to 100 recovery capacity of the conventional example A which consists of the conventional composition, and consists of each composition. As compared with the conventional example A, the example B1 of this invention and B-2 are remarkable, and capacity was falling. By the way, the effect which eases the influence of the passivity film generated to the interface of a lattice body and an active material after overdischarge neglect with the effect that the Sb layer on the surface of

a positive electrode grid of the conventional example A raises the charge acceptance nature described previously is known. Therefore, B1 and B-2 are considered that capacity fell without the ability to recover even if it is influenced by the nonconducting film of the interface generated by overdischarge neglect and charges. On the other hand, capacity with the examples C1 and C2 of this invention equivalent to the conventional example A was obtained. This can presume being able to consider the effect as the Sb layer of the conventional example A that the Sn layer on the surface of a positive electrode lattice body in the examples C1 and C2 of this invention is the same, and easing the influence of the nonconducting film of the generated interface.

[0026]As mentioned above, in the part except the connection body which does not contain Sb in an anode but to which a negative electrode connects between cells, the shelf which welds a polar plate, and a polar-plate handle part, To the amount of negative electrode active material, the lead storage battery of composition of carrying out controls the increase in **** at the time of the life cycle which is a technical problem, and cancels the corrosion in a negative electrode, and 0.001 mass %-0.1 mass % content contributes the outstanding life performance for Sb. The lead storage battery of the above-mentioned composition using the anode board which assumes also in overdischarge neglect and forms the lead alloy layer on the surface of a positive electrode lattice body for which more than 2 mass % contains Sn in part at least is desirable.

[0027]

[Effect of the Invention]As mentioned above, the lead storage battery of composition of not containing Sb in an anode but containing Sb in very small quantities to the amount of negative electrode active material in a negative electrode can have the life characteristic which controlled the increase in **** at the time of a life cycle, and maintained moderate low water loss, and canceled the corrosion in a negative electrode, and was excellent. Also when overdischarge is carried out, especially as for the lead storage battery of the above-mentioned composition using the anode board which forms the lead alloy layer on the surface of a positive electrode lattice body for which more than 2 mass % contains Sn in part at least, the characteristic which prevented capacity lowering and was stabilized can be obtained.

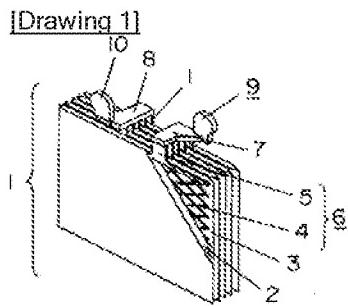
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DRAWINGS



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